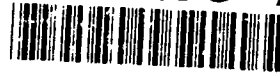


AD-A259 766



1

ESL-TR-91-32



**PHOTOPROMOTED AND THERMAL
DECOMPOSITION OF NITRIC OXIDE
BY METAL OXIDES**

E. BERMAN, J. DONG, AND N. N. LICHTIN

**PROJECT SUNRISE, INC.
1795 BEACON STREET
BROOKLINE, MA 02146**

**DTIC
ELECTE
FEB 2 1993
S C D**

APRIL 1992

FINAL REPORT

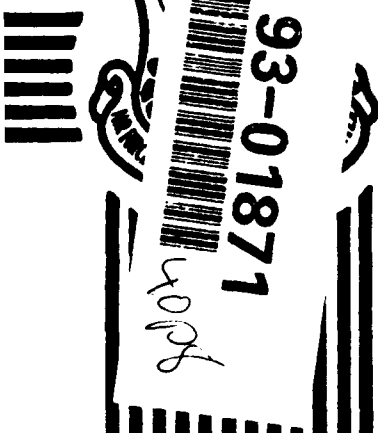
JUNE 1989 - JUNE 1991

**APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED**



**AIR FORCE ENGINEERING & SERVICES CENTER
ENGINEERING & SERVICES LABORATORY
TYNDALL AIR FORCE BASE, FLORIDA 32403**

98 2 1 097



NOTICE

PLEASE DO NOT REQUEST COPIES OF THIS REPORT FROM
HQ AFESC/RD (ENGINEERING AND SERVICES LABORATORY).
ADDITIONAL COPIES MAY BE PURCHASED FROM:

NATIONAL TECHNICAL INFORMATION SERVICE
5285 PORT ROYAL ROAD
SPRINGFIELD, VIRGINIA 22161

FEDERAL GOVERNMENT AGENCIES AND THEIR CONTRACTORS
REGISTERED WITH DEFENSE TECHNICAL INFORMATION CENTER
SHOULD DIRECT REQUESTS FOR COPIES OF THIS REPORT TO:

DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22314

1a. NAME OF FUNDING / SPONSORING ORGANIZATION HQ AFESC	8b. OFFICE SYMBOL (If applicable) RDV	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F08635-89-C-0225	
1c. ADDRESS (City, State, and ZIP Code) Tyndall AFB FL 32403-6001		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 62206F	PROJECT NO. 1900
		TASK NO. 70	WORK UNIT ACCESSION NO. 54

1. TITLE (Include Security Classification)

Photopromoted and Thermal Decomposition of Nitric Oxide by Metal Oxides (U)

2. PERSONAL AUTHOR(S)

E. Berman, J. Dong, and N.N. Lichtin

3a. TYPE OF REPORT Final	13b. TIME COVERED FROM 890612 TO 910630	14. DATE OF REPORT (Year, Month, Day) April 1992	15. PAGE COUNT 44
-----------------------------	--------------------------------------------	-----------------------------------------------------	----------------------

6. SUPPLEMENTARY NOTATION

Availability of this report is specified on reverse of the front cover

7. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Catalysis (U) Photocatalysis (U) Metal Oxides (U) NOx Removal (U)
FIELD	GROUP	SUB-GROUP	

9. ABSTRACT (Continue on reverse if necessary and identify by block number)

This technical report summarizes research on decomposition of NOx by photopromoted and thermal solid-catalyzed decomposition of NO. Typical catalysts incorporated one or more metal oxides. Photopromotion of catalytic activity was observed with several catalysts. Nearly complete thermal decomposition of NO was achieved by several catalysts in the absence of O₂. However, no combination of catalyst and conditions achieved satisfactory rates of decomposition of NO in the presence of target concentrations (>10 percent) of O₂.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL JOSEPH D. WANDER		22b. TELEPHONE (Include Area Code) (904) 283 6026	22c. OFFICE SYMBOL RAVS

EXECUTIVE SUMMARY

A. OBJECTIVE:

The objective of this effort was to develop and test a catalyst capable of removing nitrogen oxide (NO_x) from gas turbine engine (GTE) exhaust during static firing tests.

B. BACKGROUND:

Emissions of NO_x are regulated under Title IV of the Clean Air Act, earlier Federal acts and various state and local laws. Whereas a jet engine (GTE) on a moving aircraft is considered a mobile source, a GTE immobilized in a jet engine test cell (JETC) is subject to regulation as a fixed source. The exempt status that GTEs and JETCs have traditionally enjoyed is at risk of disappearing, and there is an immediate need for a technology that can control or eliminate NO_x emissions without compromising the performance and maintainability of the GTE or the operability of the JETC.

This effort is the seventh of a series of investigations of candidate technologies being explored by HQ AFESC as possible methods to control NO_x during GTE testing. Five of the previous six technologies evaluated were able to demonstrate only slow or incomplete removal of NO_x from representative exhaust streams or surrogates. The sixth program, an investigation of the intrinsic catalytic properties of vermiculite, will continue through FY 92.

C. SCOPE:

During this study, a series of mixed metal oxide catalysts were prepared, micro- and bench-scale reactors for both photo and thermal testing were constructed, and an analytical method was devised for the measurement of nitrogen dioxide in the presence of nitric oxide. Each of the catalysts was tested for capability of removing nitric oxide from surrogate exhaust streams. Data are presented for 20 catalysts.

D. METHODOLOGY:

Conventional methods were used in the preparation of the metal oxides, in analysis of nitric oxide and nitrogen dioxide using a Beckman 951A NO/NO_x analyzer, and in gas chromatographic analysis of carbon dioxide, nitrogen, oxygen and water. The placement

of catalyst in the reactor was such that it formed a plug through which all of the treatment gas stream passed.

E. TEST DESCRIPTION:

Each test consisted of charging a reactor with a catalyst, stabilizing the system at the test temperature, passage of a gas mixture through the catalyst bed (with or without illumination) and measurement of the composition of the gas mixture after treatment. The extent of removal of nitric oxide was calculated from the input and effluent concentrations of nitric oxide.

F. RESULTS:

Photoenhancement of reactivity of two- to fourfold was observed for three catalysts, but none showed sufficient reactivity to be of practical interest; however, several catalysts showed good thermal catalytic properties, therefore the later stages of the investigation pursued thermal catalysis. In the absence of added oxygen, five catalysts quantitatively decomposed nitric oxide and several more were very effective. In the presence of 13 percent oxygen, all active catalysts of the series studies were deactivated by at least an order of magnitude, and nitrogen dioxide formed as a major product.

G. CONCLUSIONS:

Both the idea of photoenhancement of catalytic activity and the idea that an appropriate catalyst should be capable of decomposing nitric oxide into nitrogen and oxygen in the presence of excess oxygen are valid, and limited success was encountered in demonstrating both. However, none of the catalysts tested in this study performed at a practical level.

H. RECOMMENDATION:

A better understanding of the details of the mechanism of oxygen desorption from the catalyst surface would substantially aid the selection of more useful catalysts.

PREFACE

This report was prepared by Project Sunrise, Inc. (formerly Synlize, Inc.) of 1795 Beacon Street, Brookline, MA 02146 under Contract No. F08635-89-C-0225, from the US Air Force Engineering and Services Center, Engineering and Services Laboratory (HQ AFESC/RD), Tyndall Air Force Base, Florida 32403-6001.


This report summarizes work done between 12 June 1989 and 30 June 1991, under the direction of Dr. Norman N. Lichtin. Capt. Wayne P. Chepren and Dr. Joseph D. Wander were the Air Force project officers for this contract.

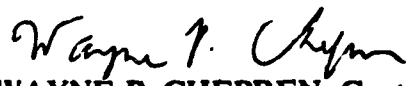
We wish to acknowledge with thanks the cooperation of The Chemistry Department of Boston University and its chairman, Dr. Guilford Jones.

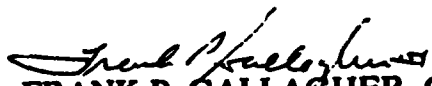
This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for public release.


JOSEPH D. WANDER
Project Officer


NEIL J. LAMB, Lt. Col., USAF, BSC
Chief, Environics Division


WAYNE P. CHEPREN, Capt., USAF
Chief, Environmental Compliance
R&D Branch


FRANK P. GALLAGHER, Col., USAF
Director, Engineering and Services
Laboratory

(The reverse of this page is blank)

v

DTIC QUALITY INSPECTED 3

Accession For	
NTIS	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist	Special

A-1

TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION.....	1
	A. OBJECTIVE.....	1
	B. BACKGROUND.....	1
	C. SCOPE.....	4
II	EXPERIMENTAL.....	7
	A. DESCRIPTION OF APPARATUS.....	7
	B. PREPARATION OF CATALYSTS.....	17
	C. EXPERIMENTAL PROCEDURE.....	20
	D. EXPERIMENTAL RESULTS.....	21
	E. DISCUSSION OF EXPERIMENTAL RESULTS.....	27
III	CONCLUSIONS.....	29
	REFERENCES.....	31

LIST OF TABLES

Table	Title	Page
1	NO _x CONVERSION IN THE STATIC PHOTOREACTOR.....	22
2	NO _x CONVERSION UNDER STANDARD THERMAL CONDITIONS	23
3	NO _x CONVERSION UNDER REDUCTION CONDITIONS.....	25
4	NO _x CONVERSION IN THE FLOW PHOTOREACTOR.....	26
5	KEY TO CATALYST NUMBERING SYSTEM.....	26

LIST OF FIGURES

1	The Static Photoreactor System.....	8
2	The Thermal Catalytic Reactor System.....	10
3	The Thermal Catalytic Reactor System Schematic.....	11
4	The Thermal Catalytic Reactor.....	12
5	The Photocatalytic Flow Reactor.....	15
6	The Photocatalytic Flow Reactor.....	16

SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this investigation was to prepare and evaluate mixed metal oxides as catalysts for removal of nitrogen oxides (NO_x) from gas turbine engine (GTE) exhaust during static testing in jet engine test cells (JETCs).

B. BACKGROUND

1. Requirement for Technology to Control NO_x .

The Department of Defense has directed its components to ensure that their operations are conducted in compliance with all applicable environmental regulations (Reference 1). NO_x standards have traditionally not been enforced for JETCs, which qualify for regulation as fixed sources, or for GTEs operating as mobile sources. Evolving regulations, including Title IV of the Clean Air Act Amendments, the failure of existing controls on stationary industrial processes to significantly lower urban ozone concentrations, and demonstrated correlation of ozone levels with NO_x concentrations (Reference 2) point to increasing pressure to limit the emission of NO_x from JETCs.

In addition to the imminent regulation, the observability of NO_x in the exhaust plume of a jet aircraft is an operational liability because it provides a mechanism for tracking and targeting the aircraft. Engine emissions will eventually be decreased by design changes to engines and fuels. However, during the service lifetime of the present generation of GTEs (about 20 years), some form of NO_x control will probably be needed to ensure compliance with impending environmental regulation.

Present technology for removal of NO_x from combustion streams operates fairly well under steady-state conditions. However, an operating JETC varies from zero flow between tests to a periodically varying exhaust stream corresponding to engine settings ranging from idle to operation of the afterburner under full military power. Within the span of a few minutes, flow rates, gas temperatures and component concentrations of the stream may vary by factors of two or more. In addition, introduction of significant resistance to airflow in the JETC will destroy the pattern of circulation. A criterion for success in this series of

investigations is that the NO_x -removal system may not create a pressure drop exceeding 3 inches of water.

Although emissions representative of the operation of a number of GTEs in JETCs have been measured (References 3-6), these data are not significant to the test process, so treatment of pollutants need not interfere with the function of the JETC. Marginal success has been encountered in applying selective catalytic reduction (SCR) to JETCs, but the process is sensitive to changes of composition and temperature in the process stream, and the application of SCR would require complicated and expensive process control devices to avoid either undertreatment of NO_x or releases (slip) of ammonia. In addition, the flammability and toxicity of ammonia present consequential risks at storage and application sites.

Six other studies of candidate NO_x -control concepts have been supported by HQ AFESC during the early stages of this investigation. Reburning with extra fuel was shown to be effective but economically impractical (Reference 7), and cause disproportionation of NO into N_2 and NO_2 (Reference 8). Expansion on a Japanese patent (Reference 9) showed efficient removal of NO_x by reduction at the surface of Group IIA oxides (Reference 10), but the toxicity of the heavy metals involved is a matter of concern.

Ceramic supported electrocatalysts were effective in the absence of oxygen, but the extent of conversion falls off very quickly as traces of oxygen are added (Reference 11); if the selectivity of binding of NO in the presence of oxygen can be increased by one to two orders of magnitude, this may be a practical technology. A dual bed mordenite-copper mordenite SCR catalyst was shown to offer some improvement in sensitivity to variability of conditions over existing SCR catalysts (Reference 12). In the sixth study, which continues through 1992, vermiculite (Reference 13) achieved removal of about half the NO from combustion streams over a range of temperatures; pretreatment of the vermiculite with several of a series of organic and inorganic materials greatly enhanced the extent of removal; these catalysts may also benefit from double-bed formulations.

2. Interactions of Photons with Metal Oxides.

Photoeffects at gas-solid interfaces and on catalysis by solids are subjects of long-standing scientific interest. (See References 14 and 15 for reviews and Reference 16 for

a study of photoeffects on the interaction of $N^{18}O$ with titanium dioxide.) The results of research in these two areas suggest two approaches for selecting catalysts and conditions for their use. One is to use radiation in conjunction with catalysts of known but insufficient catalytic activity in the thermal decomposition of NO. The other is to apply the "photoelectrochemical" model of photopromotion of catalysis (References 17 and 18). These two approaches are elaborated below.

The work of Winter on thermal catalytic decomposition of NO over metal oxides (References 19 and 20) provided a convenient departure point for planning research. In a study involving 40 metal oxides, Winter found reproducible catalytic action with 30 of them over temperature ranges that fell between 330°C and 870°C. Oxygen was found to retard decomposition of NO. Winter concluded from the observed retardation, as well as from other data, that desorption of oxygen plays a key role in governing the rate of the reaction. The mechanism that he proposes assumes that NO is adsorbed on " R_2 " sites (adjacent anion vacancies each containing a trapped electron), and that desorption of oxygen regenerates these sites. Absorption of radiation by semiconductor oxides was expected to increase the surface concentration of R_2 sites. However, recent research on photosorption processes in metal oxides (Reference 14) indicates that the situation is too complex to allow reliable prediction of conditions for photopromotion of desorption of oxygen.

The photoelectrochemical model of photopromotion of catalytic action treats semiconductor particles, under irradiation at wavelengths that they absorb, as microdiodes, which offer both anodic and cathodic surface regions to the surrounding media (Reference 18). The complete model is directly applicable only to systems in which semiconductor particles are in contact with an electrolyte. However, its concepts have been useful in predicting and rationalizing photopromoted catalysis in reactions of gases (Reference 15) and this approach is employed in what follows. Assuming that a semiconductor catalyst is in contact with liquid water or an aqueous electrolyte, the decomposition of NO can be analyzed in terms of two assumed half-cell redox reactions and their corresponding standard potentials (Reference 21), reactions 1-3:



According to the model, with an n-semiconductor, oxidation will take place at an irradiated surface and reduction at a dark surface of a catalytic particle. The potential available for the reduction is approximately the potential at the bottom of the conduction band, i.e., approximately the flat-band potential of the n-semiconductor. Since for most n-semiconductors the flat-band potential is negative of the values indicated in equation (1), this requirement is easily met. The maximum potential available for oxidation is the potential at the top of the valence band at the interface of n-semiconductor and electrolyte; it should be near to or more positive than the potential of reaction (2). Again, many n-semiconductors meet this requirement and at the same time inevitably meet the requirement for the flat-band potential.

With a p-semiconductor, the photoelectrochemical model predicts that oxidation will take place at a dark surface of the semiconductor and the potential available for oxidation is approximately that of the top of the valence band (approximately the flat-band potential); reduction will occur at illuminated surfaces and the available potential will approximate the bottom of the conduction band at its interface with the medium. The potential requirements of reactions (1) and (2) can be met with a number of p-semiconductors.

Application of the photoelectrochemical model implies either that catalysts are used in the form of aqueous slurries or, if only to provide an anodic reaction, that NO is exposed to irradiated catalyst in the presence of water vapor. Many n-semiconductors have potentials at the top of their valence bands that are positive enough to oxidize water, e.g., n-titanium dioxide, approximately +3V at pH 2.1, bandgap = 3V and n-ferric oxide, approximately +1.8V at pH 9, bandgap = 2V (Reference 22).

C. SCOPE

1. Preperformance goals.

Research and development work was proposed on new technology for control of emission of NO_x from jet engines undergoing testing. The technology is based on

photopromoted solid-catalyzed decomposition of NO into N₂ and O₂ prior to discharge of the exhaust stream into the atmosphere. The initial phase of the project, devoted to identification of catalysts and conditions that result in rapid decomposition of NO in gas streams having compositions similar to jet-engine exhaust, was divided into two parts:

a. The first objective was to document feasibility of the process by identifying one or more catalysts and sets of conditions that result in decomposition of at least 90 percent of the NO initially present in the gas stream during a contact time of no more than 1 second, while retaining at least 50 percent of initial steady-state catalytic activity for at least 1 hour, and that suffers no more than a 10 percent decrease in initial rate of decomposition or catalytic stability when the gas stream includes O₂ amounting to as much as 20 mole percent of initial NO. Catalysts were chosen on the basis of one or more criteria: (1) photoactivation of metal oxides known to display significant but insufficient activity in catalyzing the thermal decomposition of NO, and (2) metal oxides with semiconductor properties that, according to the photoelectrochemical model of catalysis by semiconductors, should result in the desired activity. In addition, components that promote release of O₂ were incorporated in the catalysts.

b. The second objective was to improve the performance characteristics of the process to a level compatible with the subsequent development of an NO control device for jet engines operating under test bed conditions. These characteristics include decomposition of 99 percent of NO in the gas stream, during a contact time no greater than 1 millisecond, retention of at least 50 percent of initial steady-state catalytic activity during 10 hours of use, and insensitivity to O₂ similar to that specified in IC1a.

2. Goals added during the contract.

After the briefing held at Tyndall Air Force Base on March 2, 1990, the following additional goals were added:

a. Model systems will be constructed and used in further evaluation and optimization of efficiency of catalyzed thermal decomposition of NO_x. These systems will be scaled up 10-100 fold compared to the microflow reactors used during the first year. They will provide for measuring NO_x decomposition in gas mixtures (including soot) approximating compositions of jet exhaust at temperatures and space velocities

corresponding to catalytic treatment either in the exhaust cowling of jet engines or downstream in the expansion tunnels of test modules or hush houses. Chemical compositions of model gas streams will be monitored before and after catalytic treatment. Treatment in the jet exhaust cowling will be modeled by catalyst deposited on the walls of voids in honeycomb structures mounted in reactors normal to the direction of gas flow. Pressure drops across catalyst heads will be monitored.

b. Evaluation studies will be performed with those catalysts that are shown to be the most promising during the first year. At the time of the briefing it appeared that these included platinized lanthanum-nickel-oxide preparations, possibly platinized or unplatinized lanthanum nickel titanium oxides, copper nickel oxides on titanium dioxide and on aluminum oxide, and possibly the latter catalysts modified with platinum or rhodium.

c. Promising catalysts will be characterized before and after use by determining elementary composition, X-ray powder diagrams, ESCA spectra, surface area and, for surface-modified catalysts, surface morphology as measured by SEM.

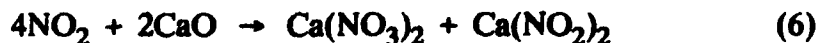
SECTION II EXPERIMENTAL

A. DESCRIPTION OF APPARATUS.

1. Static Photocatalytic Reactor System.

The static reactor system shown in Figure 1 consists of four parts: a 150-w quartz halogen lamp, its focusing and cooling accessories and an IR filter (the total output of the lamp was 9.4×10^{16} photons/sec. in the wavelength range of 350-480 nm, as determined by chemical actinometry); a vacuum line composed of a mechanical pump, a mercury manometer and an NO_x trap; a photocatalytic reaction cell and a temperature controller. The reaction cell, unless specified otherwise, was a Pyrex® rectangular flask 80x40x20mm. The cell was buried in a furnace except for one face through which radiation was admitted. Pressure monitoring was carried out with an electric manometer in which the mercury level was proportionally converted to an electrical signal and charted by a plotter.

The following reactions take place in the reaction cell which is operated under a nitrogen atmosphere:



and the overall reaction is:



Both calcium nitrate and nitrite are stable compounds that have negligible vapor pressure under the temperatures investigated. The overall reaction results in a decrease in pressure with four molecules of NO leading to the formation of one molecule of nitrogen. Thus, the reaction can be monitored by the pressure change in the system. Only two of the four nitric oxide molecules are catalytically decomposed, while the other two are consumed by combination with oxygen so that the theoretical rate of photoassisted catalytic decomposition should be half of the measured rate. The total pressure P_t at time t , with initial NO pressure of P_0 and NO partial pressure P at any time, follows the relation:

$$P = 1/3(4P_t - P_0)$$

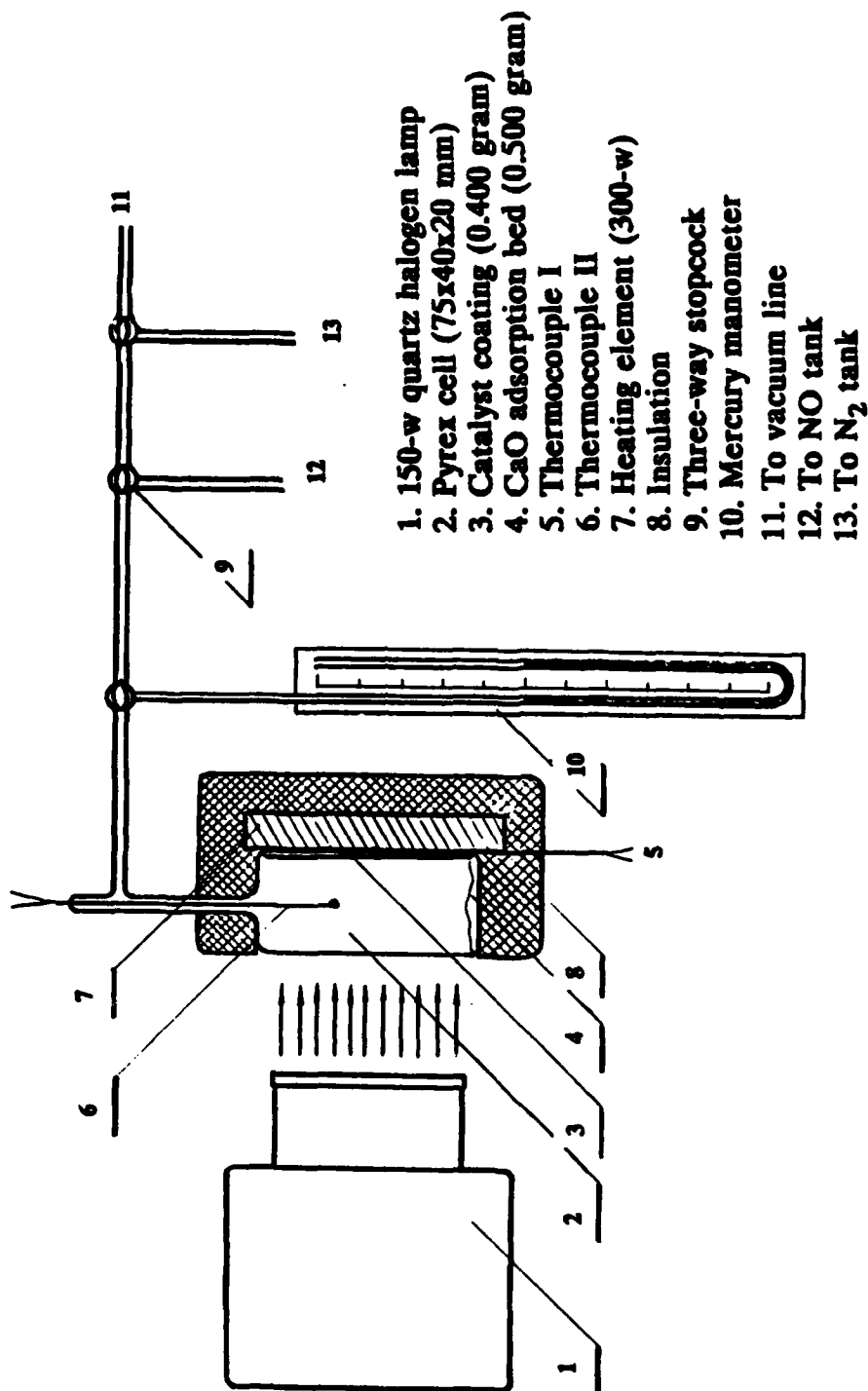


Figure 1. The Static Photoreactor System

which holds if there are other inert gases such as nitrogen and argon at the start of the reaction, except that the initial partial pressure of these species must be subtracted from the total pressure P_t .

Kinetically, reactions 5 and 6 are fast, half-life times being less than one second when P_{NO} is above 10 torr, as determined by experiment. Reaction with pure NO and O_2 over a CaO bed in the same reaction cell under different conditions, showed that the time for quantitative completion was less than 15 seconds, while the half-life time of photoassisted catalyzed decomposition of NO under similar conditions was greater than one hour. Thus it was concluded that the pressure change of the system actually represents the rate of catalytic NO decomposition.

2. Thermal Catalytic Reactor System for NO_x Decomposition.

The thermal catalytic reactor system for NO_x decomposition is shown in Figures 2, 3 and 4. It consists of three major parts: gas mixing, catalytic NO_x decomposition and composition analysis.

In the gas-mixing stage, N_2 (WESCO, grade 4.0), CO_2 (Matheson, high purity grade), 1 percent NO in N_2 (both Matheson high purity grade), 0.1 percent to 1 percent CO in CO_2 (Matheson high purity grade), and O_2 (WESCO, grade 3.0) were regulated via gas flow controllers (Tylan Model RO-28) at different ratios to make the desired compositions. The mixed gas was then passed through a water evaporator to be saturated with water vapor. The content of water vapor could be adjusted in the range of 1 percent to 20 percent by adjusting the temperature of the water bath (Thermostat Neslab Model RTE-220) in which the evaporator was placed. The actual flow rate for each individual gas as well as the total flow was calibrated by a soap bubble flow meter.

The stainless steel catalytic reactor was 25 mm in internal diameter and 800 mm in length with Swagelok connectors and reducers. The reactor was packed with 2-mm diameter quartz chips. The catalyst powder (200 mesh) was shaken into 0.3-0.5 mm of quartz wool and sandwiched between two layers of quartz wool (each 10 mm in length) to prevent migration of the powder. The overall length of the reactor was divided into three zones: preheating (650 mm), reacting (30-50 mm) and stabilizing (100-200 mm). A chromel-alumel thermocouple (Omega Type K) was pinned to the center of the catalyst bed and

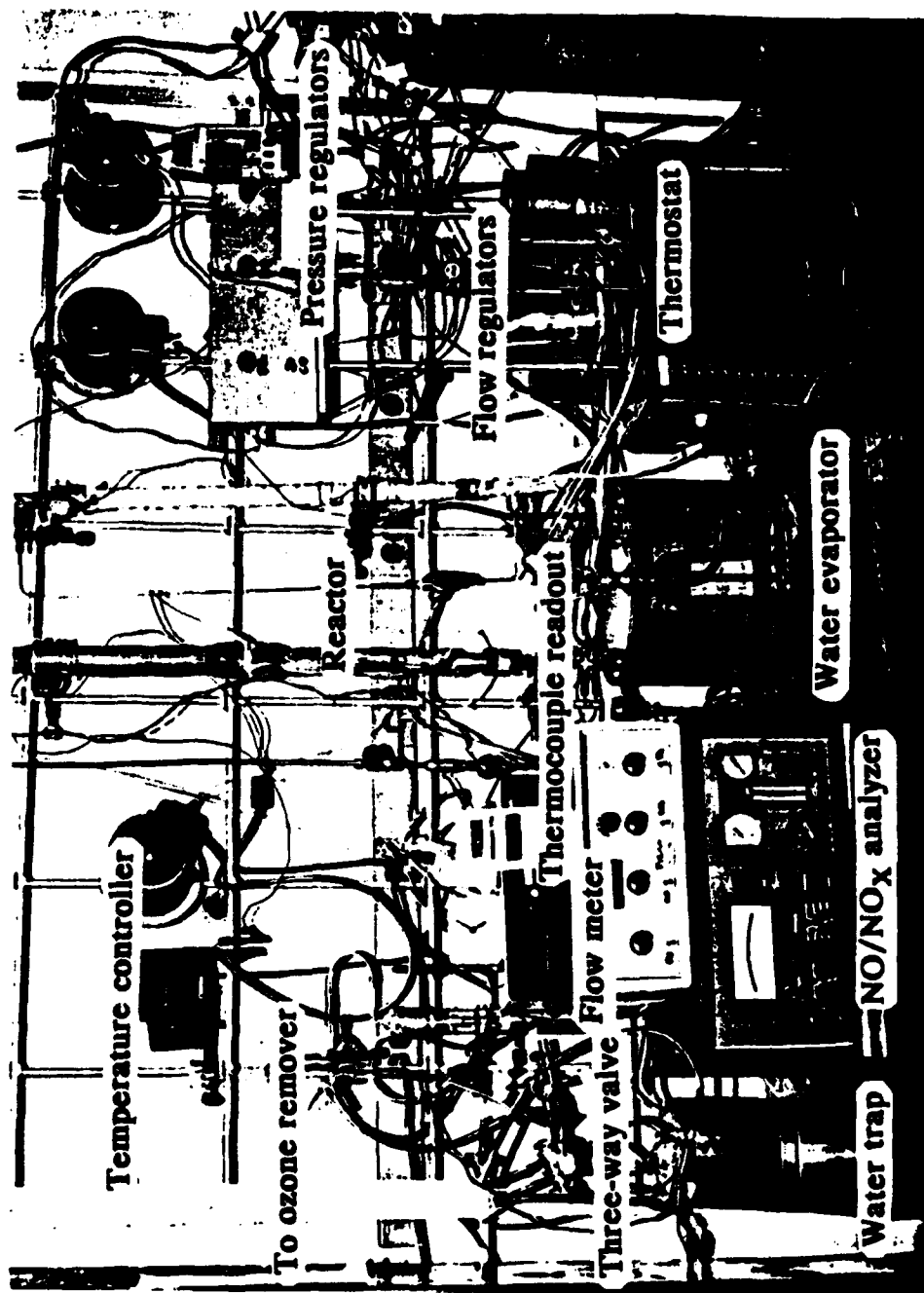


Figure 2. The Thermal Catalytic Reactor System

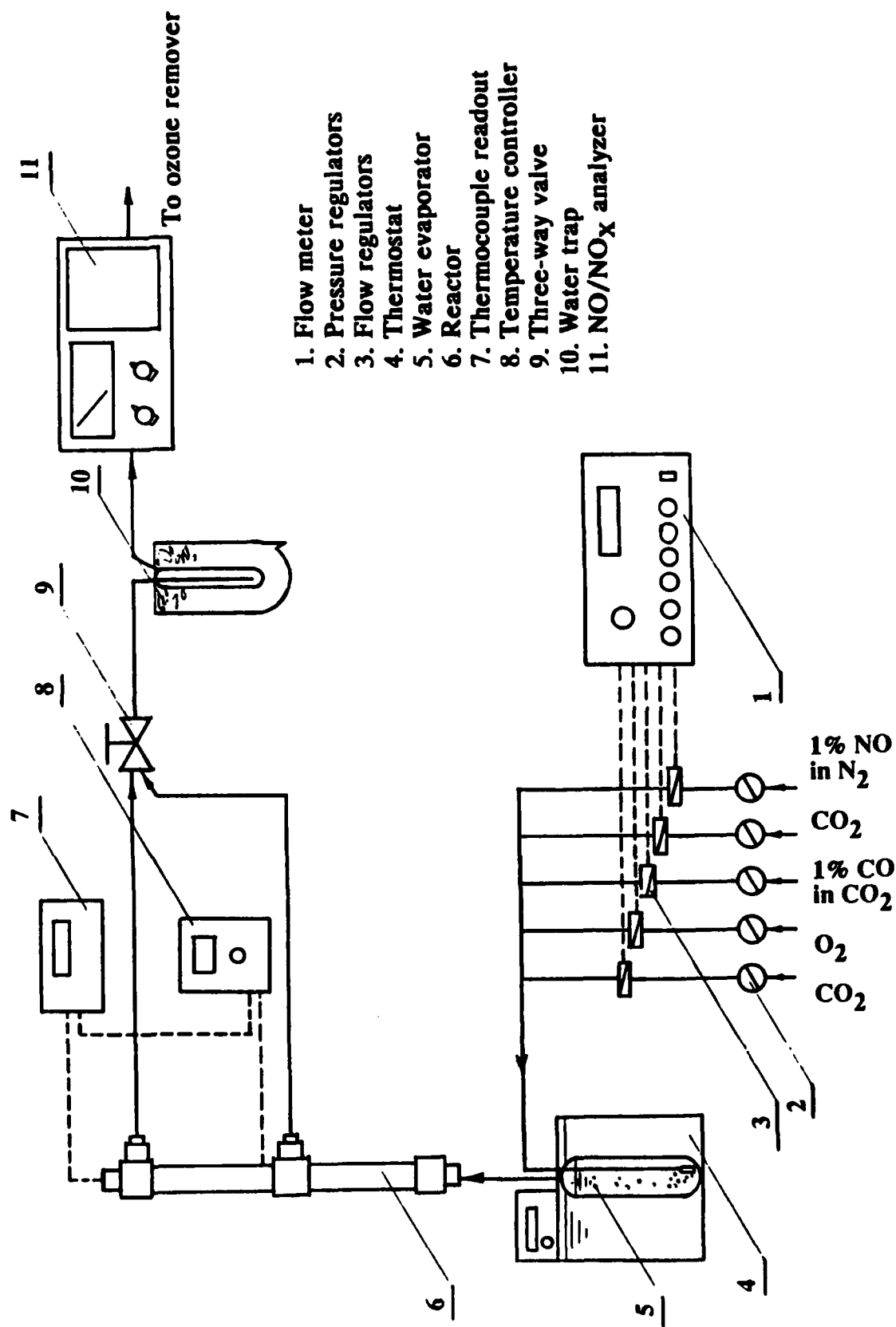


Figure 3. The Thermal Catalytic Reactor System Schematic

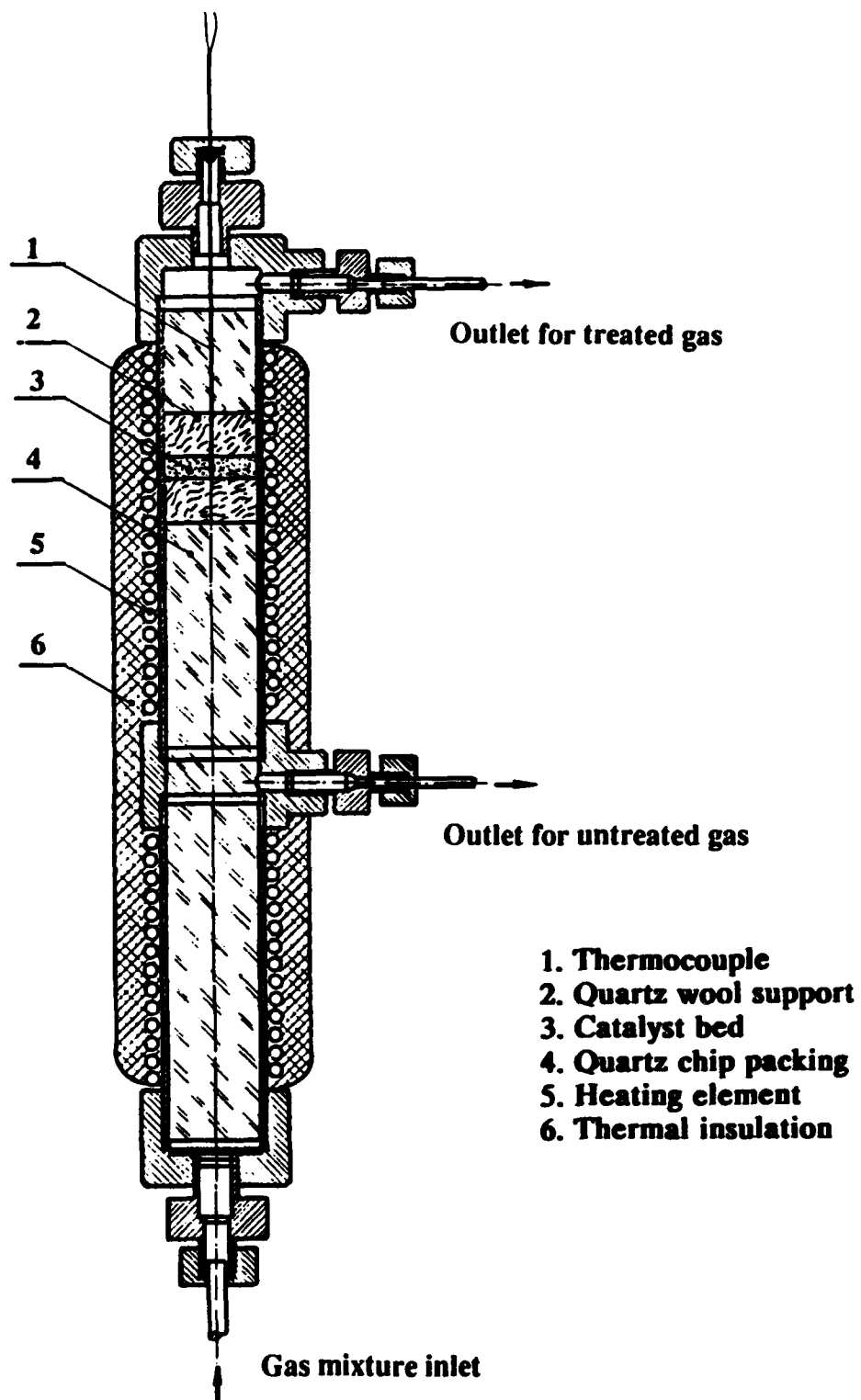


Figure 4. The Thermal Catalytic Reactor

coupled with a temperature controller (Omega CN7001R1) and a digital thermometer (Barnant 115). Heating was provided by an 800-watt high-temperature heating tape. The full unit was wrapped in Vycor® wool fabric to prevent heat loss and to assure uniform temperature distribution. The gas mixture was introduced into the bottom of the reactor and proceeded up the reactor where it underwent heating and contact with the catalyst. The treated gas was tapped out from the top of the reactor via a three-way connection and unreacted gas could also be sampled from the middle of the reactor by switching a three-way valve in the reaction system. Stainless steel tubing (1/4 and 1/8 inch) and connectors were used wherever NO_x was likely to be present; the remainder of the plumbing was done with copper tubing.

The exit gas from the reactor was dehumidified to less than 0.5 percent water content in a condenser before being moved to the NO/NO_x analyzer (Beckman 951A). The exhaust was vented into an ozone remover (Oriel 66087), then to an exhaust hood. Gas chromatography (Perkin-Elmer Sigma 300) was periodically used to check the oxygen, carbon dioxide, nitrogen and water concentration on a molecular sieve and Porapak® Q column combination.

3. The Microthermal Catalytic Reactor System.

The microthermal reactor was of similar construction to the thermal catalytic reactor system with dimensions approximately one third of those of the thermal catalytic reactor. The catalyst powder (0.2 grams) was placed directly on top of the glass chip packing and it was assumed that the powder occupied a minimal volume leading to very high calculated space velocity. A major difference between the two systems was in the analytical method employed. For the micro reactor, gas chromatography alone was used. NO concentrations below a few hundred ppm could not be quantitatively analyzed. Experiments were carried out with about 1 percent NO in either nitrogen or a mixture of nitrogen, carbon dioxide and air.

4. The Photocatalytic Flow Reactor System.

The flow photocatalytic reactor system has its own gas mixing and analyzing set up paralleling that of the continuous thermal catalytic reactor system shown in Figures 2 and 3. The photoreactor is shown in Figures 5 and 6. It consists of two 340-mm coaxial Pyrex®

glass cylinders having internal diameters of 60 mm and 40 mm. Catalyst is coated on the internal wall of the outer shell from a water--catalyst slurry. A cooling water jacket was placed into the axial center to house the bulb (300 w quartz halogen, LOA). The fully assembled reactor is shown in Figure 6. The overall volume between the two cylinders is 210 mL and the catalyst coated area is approximately 500 cm². The gas mixture was introduced into the reactor from the bottom and ducted out the top. A three-way valve was used to bypass the reactor for collection and analysis of the inlet sample.

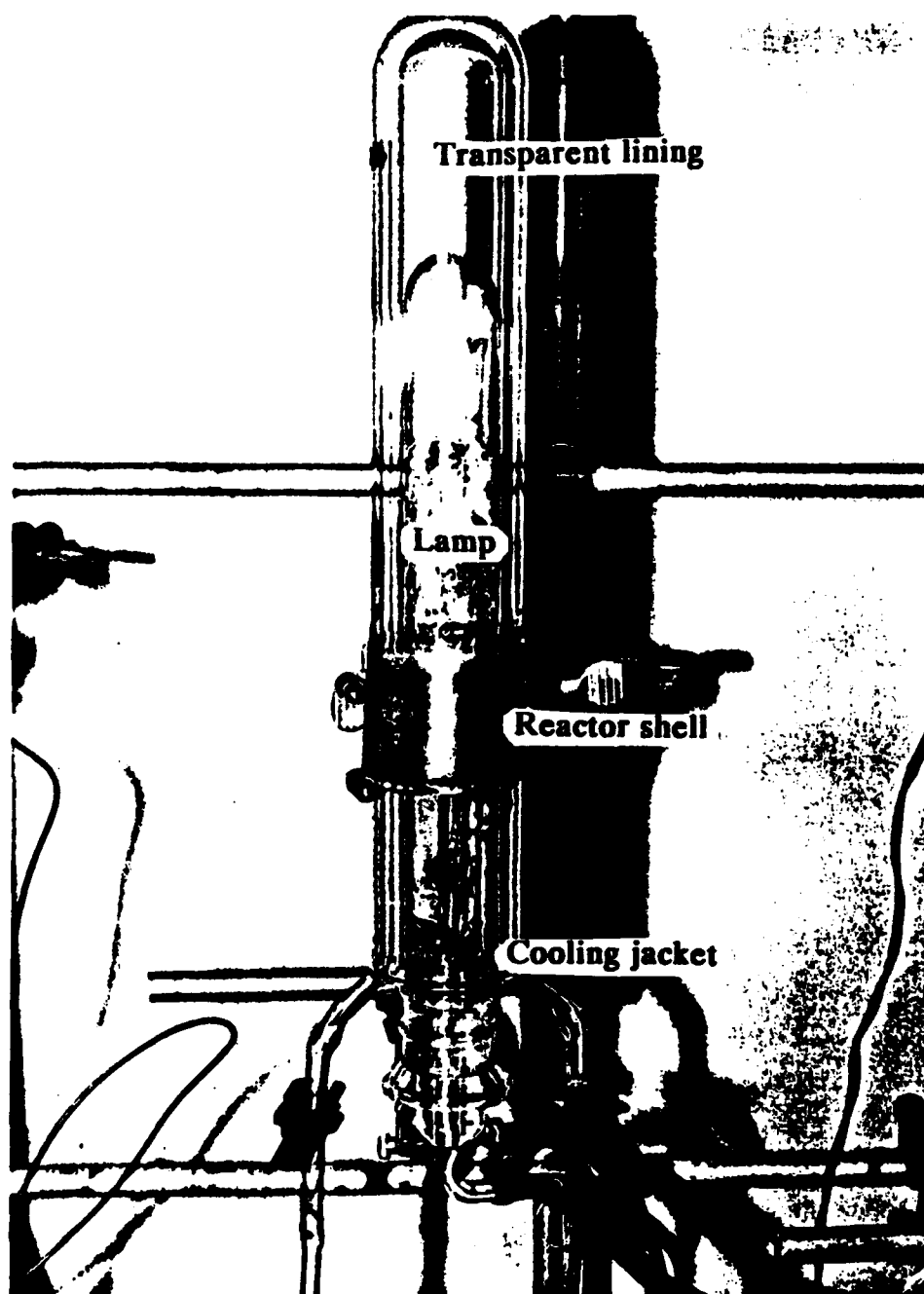


Figure 5. The Photocatalytic Flow Reactor

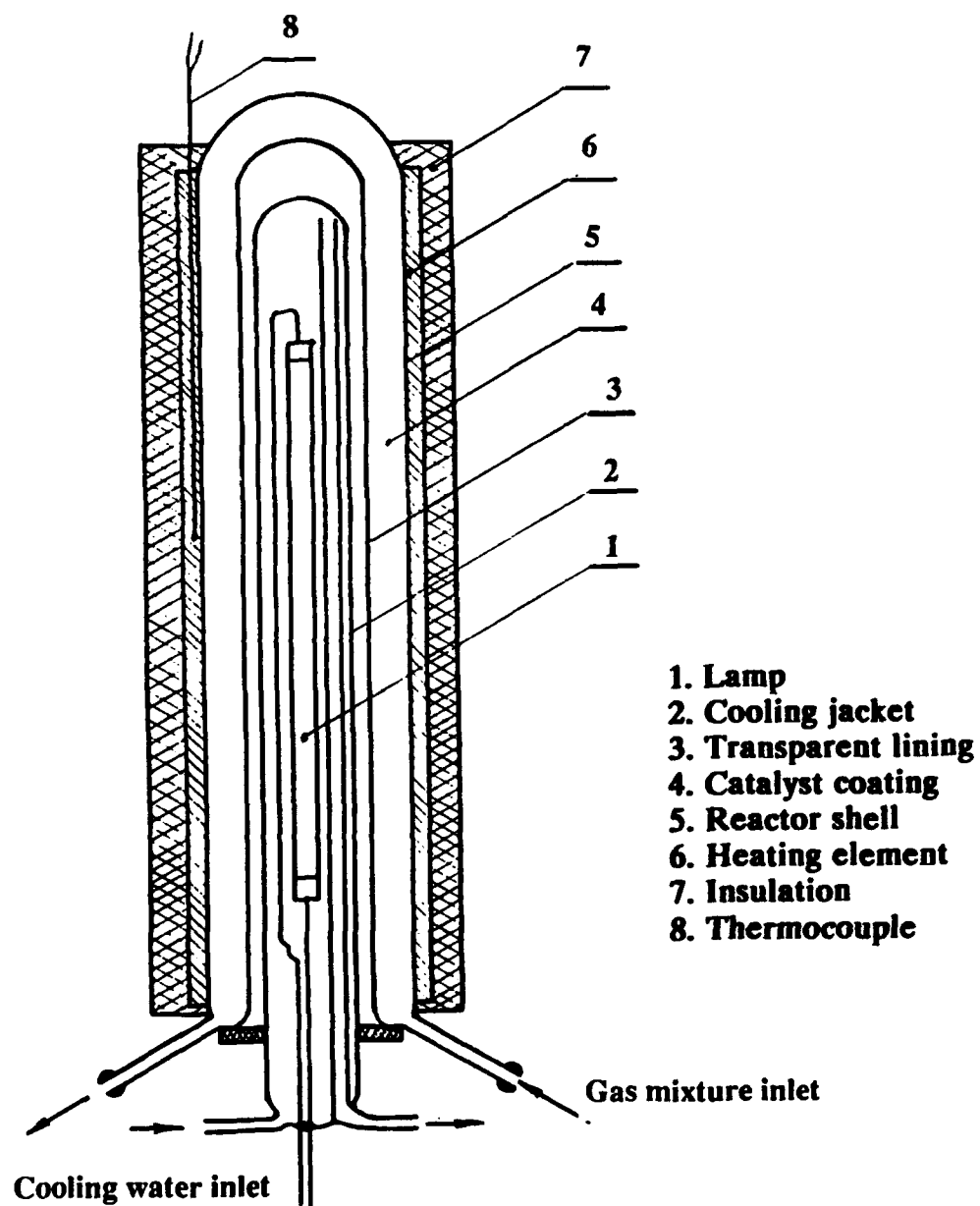


Figure 6. The Photocatalytic Flow Reactor

B. PREPARATION OF CATALYSTS.

1. Lanthanum Nickel Oxide (84)

A solid solution of lanthanum nickel nitrate was prepared by melting 88.15 grams of lanthanum nitrate hexahydrate on a steam bath and adding 59.23 grams of nickelous nitrate hexahydrate to the melt. The solid solution was dried overnight at 100°C, then heated to 120°C, cooled, ground in a mortar and pestle, and decomposed by heating at 150-200°C for 2 hours. The temperature was then raised to 600°C and maintained at 600°C for 3 hours. The material was heated in an oxygen atmosphere at 750°C for 2 days, initially interrupting the heating at the end of 2 hours to grind the material. The final material was ground again to 200-mesh before use.

2. Platinized Lanthanum Nickel Oxide (684)

A paste was made of 10.0 grams of lanthanum nickel oxide and 4.7 mL of methanol containing 2.5 mg of chloroplatinic acid (Johnson Matthey, 40 percent Pt) and dried for an hour at 100°C. The resultant solid was heated in a hydrogen atmosphere at 250°C for 2 hours and cooled overnight in hydrogen atmosphere. The product was swept with argon, then with air.

3. Titanium Dioxide (0)

Degussa Corporation P-25 grade titanium dioxide, with surface area reported by the manufacturer as 100 m²/g, was used as received.

4. Copper Nickel Titanium Dioxide (340)

To 9.0 grams of Degussa P-25 was added 3.675 grams of cupric nitrate hexahydrate and 0.51 grams of nickelous nitrate hexahydrate in 25 mL of methanol. The slurry was dried overnight at 100°C. It was decomposed at 200°C for 2 hours, then the temperature was gradually raised to 500°C and maintained at 500°C for 4 hours. After grinding to 200-mesh, the material was used without further preparation.

5. Platinized Copper Nickel Titanium Dioxide (6340)

A paste made of 10.0 grams of copper nickel titanium dioxide and 4.3 mL of methanol containing 25 mg of chloroplatinic acid was dried for 1 hour at 100°C, the resultant solid heated at 250°C in a hydrogen atmosphere for 2 hours, cooled overnight and ground to 200-mesh powder in a mortar and pestle.

6. Platinized Titanium Dioxide (60)

To 10.0 grams of Degussa P-25 titania was added 2.5 mg of chloroplatinic acid (Johnson Matthey, Pt 40 percent) in 25 mL of methanol. The slurry was irradiated with a Xe--Hg lamp at room temperature with magnetic stirring until it turned grey (2 hours) and then dried at 100°C.

7. Rhodiumized Titanium Dioxide (70)

This preparation corresponds to IIB.6. except that 2 mg of rhodium chloride hydrate (Aldrich, Rh 50 percent) was substituted for the chloroplatinic acid.

8. Platinized Rhodiumized Titanium Dioxide (670)

To 10.0 grams of Degussa P-25 titania was added 25 mg of chloroplatinic acid (Johnson Matthey, Pt 40percent) in 25 mL of methanol. The slurry was irradiated with a Xe--Hg lamp with magnetic stirring until it turned grey (2 hours), then mixed with 2 mg of rhodium chloride hydrate (Aldrich,Rh 50 percent) in 5 mL of methanol and irradiated again for 2 hours. The final slurry was dried at 100°C.

9. Silverized Titanium Dioxide (90)

To 10.0 grams of Degussa P-25 titania was added 17 mg of silver nitrate in 1 mL of methanol. The slurry was irradiated with a Xe--Hg lamp until it turned reddish-pink and dried at 100°C.

10. Platinized Silverized Titanium Dioxide (690)

The preparation corresponds to IIB.8. substituting 17 mg of silver nitrate for rhodium chloride.

11. Silverized Rhodiumized Titanium Dioxide (970)

To 10.0 grams of Degussa P-25 titania was added 17 mg of silver nitrate in 26 mL of methanol. The slurry was irradiated with a Xe--Hg lamp until it turned reddish-pink. The slurry was then mixed with 2 mg of rhodium chloride hydrate (Aldrich, Rh 50 percent) in 5 mL of methanol and irradiated again for 2 hours with magnetic stirring. The resulting slurry was dried at 100°C.

12. Rhodiumized Lanthanum Nickel Oxide (784)

The preparation corresponds to IIB.2. substituting 2 mg of rhodium chloride hydrate in the place of chloroplatinic acid.

13. Platinized Rhodiumized Lanthanum Nickel Oxide (6784)

The preparation corresponds to IIB.2. with the addition of 2 mg of rhodium chloride hydrate.

14. Silverized Rhodiumized Lanthanum Nickel Oxide (9784)

The preparation corresponds to IIB.2. substituting 17 mg of silver nitrate and 2 mg of rhodium chloride hydrate for the chloroplatinic acid.

15. Lanthanum Nickel Titanium Oxide (840)

A mixture of 3.526 grams of lanthanum nitrate, 2.368 grams of nickelous nitrate hexahydrate and 8.000 grams of Degussa P-25 titania was melted on a steam bath. The mixture was dried overnight at 100°C and then processed as in IIB.1..

16. Platinized Lanthanum Nickel Titanium Oxide (6840)

A paste was made of 10.00 grams of 840 and 4.7 mL of methanol containing 25 mg of chloroplatinic acid and processed as described in IIB.2..

17. Aluminum oxide (1)

Cabot gamma alumina was used as received. The surface area of the material is reported by the manufacturer to be 50 m²/g.

18. Copper Nickel Aluminum Oxide (341)

To 10.0 grams of Cabot gamma alumina was added 3.675 grams of cupric nitrate hexahydrate and 0.51 grams of nickelous nitrate hexahydrate in 50 mL of methanol. The slurry was dried at 100°C. It was then decomposed at 150 - 200°C for 2 hours, the temperature gradually raised to 500°C, and maintained at 500°C for 3 hours. The final product was ground and used.

19. Iron Oxide (5)

Baker Analyzed Reagent grade ferric oxide was used as received.

20. Platinized Iron Oxide (65)

Platinum was deposited on 10.0 grams of ferric oxide (Baker) by the thermal decomposition of platinum sodium citrate containing 10 mg of platinum and dried in argon at 300°C for 1 hour.

C. EXPERIMENTAL PROCEDURE.

1. Static Photoreactor System.

For each experiment 0.6 grams of dry calcium oxide was weighed into the catalyst-coated reactor cell, and the system evacuated to less than 1 torr total pressure and filled with high-purity nitrogen and reevacuated. This purging procedure was repeated five times to bring the oxygen concentration to less than 1 ppm.

2. Thermal Catalytic Reactor System.

a. Loading, conditioning and start up.

- (1) Determine the bulk density of the catalyst.
- (2) Disperse 1 mL of the catalyst on quartz wool by dry shaking and load into the reactor. Determine the exact amount of catalyst loaded.
- (3) Purge with nitrogen for at least 10 minutes at room temperature, turn on the heater, raise the temperature and continue to purge with nitrogen.

(4) Keep the reactor at the test temperature for 30 minutes.

(5) Turn on the gases.

(6) Measure NO and NO_x in both the feed and effluent.

b. Measurement of activity as a function of temperature.

(1) With oxygen off, admit the reaction feed over the catalyst and follow the NO and NO_x out as a function of time until a steady-state value is obtained.

(2) Increase the temperature in increments of 100°C at the fixed composition and space velocity and obtain the steady-state NO and NO_x values.

(3) Cool the reactor to the lowest reaction temperature, start the oxygen flow and redetermine the steady-state values of NO and NO_x as in (1) and (2).

3. Photocatalytic Flow System.

The procedure is identical with IIC2. with the additional step of turning on the lamp when photoactivity is to be measured.

One gram of catalyst powder was placed into a vial, 10 mL of water added and the mixture was stirred to make a slurry. The slurry was poured into the reactor and the reactor rotated horizontally to coat the slurry onto the inner wall of the shell. After a uniform coating was obtained, the extra slurry was drained back into the vial, dried at

200°C and weighed to determine the amount of catalyst that had been coated. The reactor coating was dried in a pure nitrogen purge overnight at room temperature and conditioned with nitrogen at 200°C with the radiation on for 4 hours.

D. EXPERIMENTAL RESULTS.

1. Closed Photocatalytic System.

The data given in Table 1 are for tests run in an 84-mL closed reactor at 250°C with radiation from a 150-w quartz halogen lamp, catalyst coating of 12.5 mg/cm², and starting NO pressure of 8, 40, 100, 300, and 750 torr.

2. Thermocatalytic Systems.

a. The data given in Table 2 were generated in the thermal reactor under the following conditions: Flow of 500 mL/min; NO = 100 ppm; CO = 13 ppm CO₂(v) = 3.5 percent; O₂(v) = 13 percent; H₂O(v) = 10 percent; N₂ = Balance; Temperature was varied.

b. The data given in Table 3 were generated in the thermal reactor under the following conditions: Flow of 500 mL/min; NO = 100 ppm; CO(v) = 0.55 percent(I); 0.85percent(II); 1.14 percent(III); CO₂(v) = 10 percent; H₂O(v) = 10 percent; O₂(v) = 0.5 percent; N₂ = Balance; Temperature was varied. Reducing ratios of O₂/CO: 0.88/1(I); 0.88/1.5(II); 0.88/2(III).

TABLE 1 NOx CONVERSION IN THE STATIC PHOTOREACTOR

CATALYST*	THERMAL RATE CONSTANT k_t First order hr^{-1}	PHOTOASSISTED RATE CONSTANT k_p First order hr^{-1}	k_p/k_t
5(Fisher)	0.18	0.53	3
5(Baker)	0.18	0.80	4.5
0	0.004	0.012	3
60	0.40	0.88	2.2
4	0.37	0.42	1.1
684	2.34	2.45	1.05
65	1.09	0.97	0.89

*Catalysts are identified by a numbering code given in Section II B. and TABLE 5. The significance of additional coding letters and numbers is to distinguish catalyst results of different preparations of the same catalyst.

TABLE 2 NOx CONVERSION UNDER STANDARD THERMAL CONDITIONS

CATALYST	TEMP °C	PERCENT CONVERSION	
		0 percent O ₂	13 percent O ₂
0	364	0	18
0	370	0	20
0	582	0	21
0Jα041B	355	0	4
0Jα040A	340	20	3
340Jα050	378	0	15
340Jα051	307	0	n/a
	460	0	0
	528	0	n/a
	645	6	n/a
340Fα048	347	32	24
	350	0	n/a
	360	0	22
	443	n/a	18
	595	25	12
	640	24	7
6340Jα058	380	9	0
	600	4	n/a
60Fα007	363	4	n/a
	364	15	n/a
	366	14	n/a
	360	16	n/a
	365	14	n/a
	355	100	20
	493	n/a	19
60Jα053	372	7	20
60Fα008B	330	31	n/a
	345	n/a	6
	455	n/a	10
70Jα055	390	30	0
670Jα056	355	43	n/a
	390	51	13
	451	100	n/a
	480	98	7
	540	2	2
	368	46	n/a
	520	n/a	2
670Jα060A	385	10	n/a
	608	n/a	2
670Jα060B	395	8	8

**TABLE 2 NO_x CONVERSION UNDER STANDARD THERMAL CONDITIONS
(CONTINUED)**

CATALYST	TEMP. °C	PERCENT CONVERSION	
		0 percent O ₂	13 percent O ₂
90Ja056	363	47	n/a
	505	100	2
690Ja056	305	3	n/a
	510	15	4
970Ja061B	370	15	n/a
	550	100	10
	570	100	5
84Ja033	300	17	27
	349	13	33
	507	22	24
	635	44	21
684Fa021	357	99	28
	516	99	23
	645	99	8
684Fa021B	368	100	18
684Ja038	355	100	15
	620	78	0
684Ja059	385	100	7
684Ja024	517	96	15
	646	96	23
784Ja054	372	100	10
6784Ja059	300	n/a	37
	355	100	n/a
	360	n/a	30
	460	n/a	16
	560	n/a	8
	650	n/a	3
9784Ja061A	360	100	17
	360	100	16
	460	100	n/a
	560	n/a	9
6840Ja039	363	99	0
1	355	4	4
341Ja047	352	0	n/a
	360	n/a	14

**TABLE 2 NO_x CONVERSION UNDER STANDARD THERMAL CONDITIONS
(CONCLUDED)**

CATALYST	TEMP. °C	PERCENT CONVERSION	
		0 percent O ₂	13 percent O ₂
341Fa047	345	0	23
	495	n/a	6
65Fa077	300	0	25
	400	0	16
	446	8	12
5	290	3	20
	395	15	8
	445	33	0

Digits preceeding the letter identify the composition of the catalyst (see Table 5). The letter identifies the worker, the information following the letter the laboratory notebook where the data is located.

n/a = Not attempted.

TABLE 3 NO_x CONVERSION UNDER REDUCTION CONDITIONS

CATALYST	TEMP. °C	Percent	CONVERSION	
		I	II	III
684Ja037	304	90	n/a	n/a
	405	81	n/a	n/a
6784Ja059	425	4	25	100
9784Ja061A	423	5	71	95
	295	82	n/a	n/a
	405	98	n/a	n/a
670Ja060 (photodep.)	435	20	n/a	n/a
	417	n/a	60	100
670Ja077 (chem. dep.)	390	24	n/a	99
970Ja060	420	75	n/a	n/a
	544	0	n/a	n/a
	321	50	n/a	n/a

3. Photocatalytic Flow System.

Experiments were conducted in a newly constructed photoreactor that allowed testing to be carried out in the presence of oxygen. The work summarized in TABLE 1 on page 22 in the closed photocatalytic system depended upon oxygen as a reactant and did not allow testing to examine the sensitivity of the system to high oxygen concentrations. Platinized titanium dioxide was tested at 150°C, 220°C, 300°C and 400°C, both illuminated by a quartz halogen lamp and unilluminated. The data are given in Table 4.

TABLE 4 NO_x DECOMPOSITION IN THE FLOW PHOTOREACTOR

Catalyst	Temperature °C	Percent	Conversion
		Dark	Light
60	150	3.6	4.1
	220	6.1	9.2
	300	6.3	6.7
	400	4.0	6.4

TABLE 5 KEY TO CATALYST NUMBERING SYSTEM

Number	Meaning	Number	Meaning
0	Titanium dioxide	1	Aluminum oxide
3	Copper	4	Nickel oxide
5	Ferric oxide	6	Platinum
7	Rhodium	8	Lanthanum
9	Silver		

The catalyst is determined by the numbers appearing prior to the first letter.

E. DISCUSSION OF EXPERIMENTAL RESULTS.

1. Closed Photocatalytic System.

The data of Table 1 show the increase in rate of nitric oxide decomposition due to illumination. However, the rates are quite low. In the case of the fastest system, platinized titanium dioxide, the observed space velocity of 0.88/hr corresponds to a dwell time of over 3000 seconds compared to a first-year goal of 1 second. When we discovered high-rate thermal processes, we changed the direction of our efforts to this apparently more promising avenue.

2. Thermocatalytic Systems.

a. The data of Table 2 summarize the work carried out on thermal catalysis of the decomposition of nitric oxide under a standard set of conditions that correspond to typical exhaust gas streams from gas turbine power plants. In the absence of appreciable amounts of oxygen the rates of decomposition are quite high. The data are based on a catalyst weight of ≈ 1 gram, a volume of ≈ 0.3 -3 mL, a flow rate of 500 mL/min \approx to a space velocity of 10,000-100,000/hr or a dwell time of 0.36-0.036 sec. In the absence of added oxygen, platinized titanium dioxide, platinized rhodiumized titanium dioxide, silverized titanium dioxide, silverized platinized titanium dioxide, platinized lanthanum nickel oxide, rhodiumized lanthanum nickel oxide, platinized rhodiumized lanthanum nickel oxide and silverized rhodiumized lanthanum nickel oxide all show essentially complete conversion of NO to nitrogen and oxygen.

The goals of the program were to demonstrate the rapid decomposition of nitric oxide in the presence of oxygen amounting to 20 mole percent of the nitric oxide. In these experiments, the initial nitric oxide concentration is 100 ppm, which on decomposition would yield 50 ppm of oxygen. Thus, on running the equipment without added oxygen, we were essentially meeting the stated goals of the program.

Under real world conditions (water vapor, carbon dioxide and oxygen) our catalysts fail badly. Although water vapor and carbon dioxide appear to have no negative effects, the best results obtained in the presence of 13 percent oxygen are a meager 37 percent conversion of nitric oxide to nitrogen and oxygen. The catalyst that shows this conversion is platinum rhodium lanthanum nickel oxide, unquestionably the most expensive catalyst

tried. Under the conditions of these experiments, the nitric oxide that is not decomposed to nitrogen and oxygen is oxidized to nitrogen dioxide.

b. The data of Table 3 summarize the work carried out on the thermal decomposition of nitric oxide under "reducing conditions," i.e., conditions under which the amount of oxygen present is exceeded by the amount of carbon monoxide present. Even in the presence of a greater than 2:1 ratio of carbon monoxide to oxygen, the catalysts rapidly lose their activity. This examination under reducing conditions was carried out in the hope that our thermal catalysts would be useful for automotive exhaust treatment.

3. Flow Photoreactor System

The data of Table 4 summarize the work carried out in the flow photoreactor. Although there is a hint of an improvement in the activity in the presence of oxygen in the case of illuminated catalyst compared to unilluminated catalyst, it is not of sufficient magnitude to be highly encouraging.

SECTION III

CONCLUSIONS

The hope of this contract was to utilize a novel catalytic technique employing photoactivated semiconductors as a means to solve one of the more serious environmental problems of our age, that of nitric oxide. When air is raised to a high temperature, nitrogen and oxygen react to produce nitric oxide. Nitric oxide is produced in substantial amounts during combustion of fossil fuels in such diverse applications as power plants, internal combustion engines, home barbecues and jet engines. Nitric oxide contributes to two major environmental problems: it is oxidized in air to become acid rain and it reacts with hydrocarbons and sunlight to produce ozone and photochemical smog, a major cause of health problems for plants, animals and man in urban environments.

The Air Force is seeking technology to control or eliminate nitric oxide from test cells and hush houses on Air Force installations during routine and emergency testing of jet engines. Their sponsorship of the work reported here was encouragement to seek novel and long range approaches to United States and World problems. Although we were able to go only a small way toward the solution of the specific problem of stationary emissions of nitric oxide, the general knowledge and skills gained will be of substantial value as we develop photooxidation techniques to destroy organic pollutants.

The major technical question this work sought to answer was whether the thermodynamically favorable decomposition of nitric oxide into nitrogen and oxygen could be speeded up sufficiently by a photo and/or thermal catalyst to be used to remove nitric oxide from existing exhaust streams. The answer to the question must be qualified. Thermal catalysts were found that work and work well, but not in the presence of significant amounts of oxygen. We were unable to overcome this difficulty or find promising leads to understand this inhibition by oxygen, other than the fact that other work in these laboratories indicates that nitrous oxide is decomposed by these same catalysts without oxygen inhibition.

We believe that systems can be found to decompose nitric oxide in real world environments and that the design of suitable catalysts will be substantially aided by more

information on the intricacies of photoadsorption and desorption of oxygen from the catalysts of this study.

REFERENCES

1. Protection and Enhancement of Environmental Quality, Department of Defense Directive 5100.50, 24 May 1973.
2. Meagher, J.F., Bailey, E.M. and Olryna, K.J., "Ozone Precursor Relationships in Rural Southeastern United States," Abst. 84th Ann. Mtg. Waste Mgt. Assoc. Abst. 91-66.12 p. 98 (1991).
Parkhurst, W.J., Leer, M.T., Bernard, B.L., Waynick, J.L., Brauner, R. and Bontrager, P., "The Middle Term Ozone Study- The First Two Years," *ibid.*, 91-69.1 p. 1st.
McAllister, R.A., Sager, T.W., Gise, J.P. and Hempbill, M.W., "Importance of NO_x Control Suggested by NMOC-NO_x-O₃ Data Analysis," *ibid.*, 91-75.1 p. 114.
3. Seitchek, G.D., Aircraft Engine Emissions Estimator, ESL-TR-85-14, Air Force Engineering and Services Center, Tyndall AFB FL, 1985.
4. Spicer, C.W., Holdren, M.W., Smith, D.L., Miller, S.E., Smith, R.N., Kuhlman, M.R., and Hughes, D.P., Aircraft Emissions Characterization: TF41-A2, TF30-P103, and TF30-P109, ESL-TR-87-27, Air Force Engineering and Services Center, Tyndall AFB FL, 1987.
5. Spicer, C.W., Holdren, M.W., Smith, D.L., Miller, S.E., Smith, R.N., and Hughes, D.P., Aircraft Emissions Characterization: TF33-P3, TF33-P7, and J79-17G (Smokeless), ESL-TR-87-63, Air Force Engineering and Services Center, Tyndall AFB FL, 1987.
6. Spicer, C.W., Holdren, M.W., Smith, D.L., Miller, S.E., Smith, R.N., and Hughes, D.P., Aircraft Emissions Characterization: F101 and F110 Engines, ESL-TR-89-13, Air Force Engineering and Services Center, Tyndall AFB FL, 1989.
7. Johnson, S.A., and Katz, C.B., Feasibility of Reburning for Controlling NO_x Emissions from Air Force Jet Engine Test Cells, ESL-TR-89-33, Air Force Engineering and Services Center, Tyndall AFB FL, 1989.
8. Ham, D.O., Muniz, G., and Gouveia, M., Additives for NO_x Emissions Control from Fixed Sources, ESL-TR-89-24, Air Force Engineering and Services Center, Tyndall AFB FL, 1989.
9. Mitzusawa, S., "Method for Removing NO and SO₂ from Exhaust Gas", Japanese Patent Application, SHO53 (1978)-137891.
10. Lyon, R.K., New Technology for Controlling NO_x from Jet Engine Test Cells, ESL-TR-89-16, Air Force Engineering and Services Center, Tyndall AFB FL, 1991.
11. Petrik, M.A., Use of Metal-Oxide Electrocatalysts to Control NO_x Emissions from

Fixed Sources, ESL-TR-89-29, Air Force Engineering and Services Center, Tyndall AFB FL, 1991.

12. Kittrell, J.R., High-Temperature NO_x Control Process, ESL-TR-89-36, Air Force Engineering and Services Center, Tyndall AFB FL, 1991.

13. Nelson, B.W., Nelson, S.G., Higgins, M.O., and Brandum, P.A., A New Catalyst for NO_x Control, ESL-TR-89-11, Air Force Engineering and Services Center, Tyndall AFB FL, 1989.

14. Cunningham, J. "Radiation and Photoeffects at Gas/Solid Interfaces," in Comprehensive Chemical Kinetics, Vol. 19, Bamford, C.H., Tipper, C.F.H., and Compton, R.G., Eds., Elsevier, Amsterdam, 1984, pp.292-427.

15. Kalyanasundaram, K., "Semiconductor Particulate Systems for Photocatalysis and Photosynthesis: An Overview," in Energy Resources through Photochemistry and Catalysis, Graetzel, W., Ed., Academic Press, NY, 1983, pp.217-260.

16. Courbon, H., and Pichat, P., "Room-temperature Interaction of N¹⁸O with Ultraviolet-illuminated TiO₂," J. Chem. Soc., Faraday Trans. 1, 1980, **80**, 3175-85.

17. Wolkenstein, Th., "The Electronic Theory of Photocatalytic Reactions on Semiconductors," Advan. Catal. **23**, 157-207 (1973).

18. Bard, A.J., "Photoelectrochemistry and Heterogeneous Photocatalysis at Semiconductors," J. Photochem. **10**, 59-75.

19. Winter, E.R.S., "The Catalytic Decomposition of Nitric Oxide by Metallic Oxides," J. Catalysis **22**, 158-170 (1971).

20. Winter, E.R.S., "The Catalytic Decomposition of Nitric Oxide by Metallic Oxides II. The Effect of Oxygen," J. Catalysis **34**, 440-4 (1974).

21. Bard, A.J., Parsons R., and Jordan, J., Standard Potentials in Aqueous Solution, Marcel Dekker, Inc., NY, 1985.

22. Morrison, S.R., Electrochemistry at Semiconductor and Oxidized Metal Electrodes, Plenum Press, NY, 1980, pp. 183-7.